Thermochimica Acta 633 (2016) 37–47

Contents lists available at ScienceDirect

Thermochimica Acta

journal homepage: www.elsevier.com/locate/tca

# Additive scheme for calculation of solvation enthalpies of heterocyclic aromatic compounds. Sublimation/vaporization enthalpy at 298.15 K

Boris N. Solomonov*, Ruslan N. Nagrimanov, Timur A. Mukhametzyanov

*Department of Physical Chemistry, Kazan Federal University, Kremlevskaya str. 18, 420008 Kazan, Russia*

ARTICLE INFO

*Article history:*
Received 25 December 2015
Received in revised form 22 March 2016
Accepted 25 March 2016
Available online 26 March 2016

*Keywords:*
Heterocyclic aromatic compounds
Fusion enthalpy
Sublimation enthalpy
Solution enthalpy

ABSTRACT

Hereby we propose a method for determination of vaporization and sublimation enthalpies of heterocyclic and carbonyl-containing aromatic compounds at 298.15 K. According to this method vaporization and sublimation enthalpies at 298.15 K are determined based on enthalpies of solvation and solution. Solvation enthalpies of heteroatomatic and carbonyl-containing compounds are calculated using an additive scheme from the solvation enthalpy of closest aromatic hydrocarbon and contributions related to the exchange of CH-groups of hydrocarbon with corresponding substituent atoms or groups. Measured solution enthalpies together with calculated solvation enthalpies allowed to calculate corresponding vaporization and sublimation enthalpies at 298.15 K for a large number of heterocyclic and carbonyl-containing compounds. We have also found that in a number of cases instead of solution enthalpy in benzene at 298.15 K fusion enthalpy at the melting temperature can be used. Comparison between literature data and calculated vaporization and sublimation enthalpies demonstrates satisfactory performance of the proposed method.



## 1. Introduction

Aromatic heterocyclic compounds are an important class of organic compounds with a wide range of applications including drugs and dyes. Some heteroaromatic compounds possess carcinogenic properties and are produced as wastes from petrochemical industry, becoming serious air pollutants. Thus the research on thermodynamics of phase transition of such compounds is a subject of constant interest [1–4]. Classical approaches for vaporization and sublimation enthalpy measurements include experimental assessment of the transition from condensed to gas state which has a well-recognized problems [5]. In [6–11] we develop an alternative procedure for vaporization and sublimation enthalpy determination, which in our view lacks some of the drawbacks of conventional methods and can be successfully employed for the determination of enthalpies of phase transitions of low volatile and thermally unstable compounds. According to this method vaporization and sublimation enthalpies at 298.15 K of compounds $A_i$ ($\Delta^g_{cr(l)}H^{A_i}$) can be calculated from enthalpies of solution of solute $A_i$ in solvent S ($\Delta_{soln}H^{A_i/S}$) and solvation of $A_i$ in a chosen solvent S ($\Delta_{solv}H^{A_i/S}$), using following equations:

$$\Delta^g_1 H^{A_i} = \Delta_{soln}H^{A_i/s} - \Delta_{solv}H^{A_i/s} \quad (1)$$

$$\Delta^g_{cr} H^{A_i} = \Delta_{soln}H^{A_i/s} - \Delta_{solv}H^{A_i/s} \quad (2)$$

Solution enthalpy employed in Eqs. (1) and (2) can be assessed by direct measurement. We developed a variety of methods for solvation enthalpy determination. For example in [9,12] solvation enthalpies of various classes of organic compounds in cyclohexane are calculated from the linear dependence of solvation enthalpy value on the molar refraction of the solute. In [6,7] solvation enthalpies of aromatic compounds and their halogen derivatives in benzene were calculated using the relationship between molar refraction and solvation enthalpy from [13]. However, this approach has its limitation because correlations between enthalpy of solvation and molar refraction were observed only for a limited number of non-alkane solvents. A simpler and more universal approach for calculation of solvation enthalpy of polyaromatic hydrocarbons in various solvents is proposed in [10]. A group-additivity scheme for calculation of solvation enthalpies in different solvents of substituted aromatic compounds was proposed in our previous work [8]. The approach is based on the following principles: in contrast to the enthalpies of phase transitions, the enthalpy of solvation of aromatic compounds in most cases does not depend on the position of substituents [7] and

* Corresponding author.
*E-mail address:* boris.solomonov@kpfu.ru (B.N. Solomonov).

http://dx.doi.org/10.1016/j.tca.2016.03.031
0040-6031/